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Degradation of humic acid by ZVI based sono-Fenton as a pretreatment for reducing organic fouling likely in membrane distillation

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ABSTRACT

Zero valent iron (ZVI) being a novel initiator and catalyst for Fenton process has abilities to adsorb and partially oxidize organic impurities while using dissolved oxygen in water. The oxidation potential of ZVI is enhanced in case of addition of hydrogen peroxide and further catalyzed while using sonication. ZVI being source of Fe^{2+} ion produces •OH radical (whose oxidation potential is utmost in comparison with other oxidizing species) steadily while using H_2O_2. Since membrane distillation faces wetting problem due to either interaction of organic impurities which eventually turn into organic fouling while presence of inorganic salts in seawater (SW) may hinder degradation of organics. For this purpose, ZVI based sono-Fenton treatment was chosen to evaluate its performance for degradation of humic acid (HA) as organic foulant within SW. Concentration of hydrogen peroxide, amount of ZVI and pH were varied to get optimum results. In previous researches, Fenton worked well in acidic pH in limited other species, however here near neutral pH from 6 to 8 was tried. Even though, 67% HA degradation was successfully achieved by using 2 g/L of ZVI with 20 mM H_2O_2 at pH 6.

Keywords: Humic acid; Organic fouling; Sono-Fenton; Zero valent iron; Pretreatment for membrane distillation

1. Introduction

Climate change towards global warming and increase in population has been putting alarming situation on freshwater availability and water scarcity [1]. On the other hand, urbanization at faster pace has deteriorated water quality [2] and there are also a lot of challenges being faced by sustainable urbanization [3]. Also, growth in industrialization has also been increasing burden on clean water demand and availability. Therefore, efficient use of water and its reuse in industries [4] and sustainability in industrial water consumption and water foot-printing of different products need also to be taken into consideration while future industrial sustainability [5].

Seawater (SW) desalination through reverse osmosis (RO) membrane technology, however, has a potential to supply plenty of water in order to meet water demand [6]. However, some challenges are RO is very expensive technology mainly because of its energy demand [7]. Second, RO brine disposal has serious environmental issues [8] and polyamide membranes which are widely used are also deteriorated with changes in composition of water being treated [9]. In addition to this, pretreatment for SWRO through coagulation, dual media filtration and cartridge filtration have even left organic foulants on filter media and membranes [10].

A novel emerging membrane technology called membrane distillation (MD) which is thermally driven and can run on waste heat as well as solar heating [11] has a potential

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to deal with RO concentrated brine solutions [12]. However, some of the limitations still are significantly diminishing the performance of MD. The most prominent one is membrane wetting and MD also faces serious membrane fouling due to presence of organics such as humic acid (HA) and natural organic matter [13]. Since MD has not been tried with supplementary pretreatment on large scale, there is also space for this area of research.

Recently combined membrane and advanced oxidation processes (AOPs) have got attention because AOPs can be used as pretreatment to reduce organic matter and other contaminations in feed water for membrane process [14]. Coupling AOPs with membrane technology in pharmaceutical wastewater has also been reported these days for effective degradation and removal of organic matter in feed water for membrane process [15]. Treatment of oily wastewater has been reported to degrade organic compounds and oils as well by combined application of ultrasound and Fenton process [16]. Therefore, if combined ultrasonic and Fenton process can treat oily wastewater, that can also reduce propensity of membrane wetting in MD.

On the other hand, nanozero valent iron (NZVI) has been reported in sono-Fenton for reduction of COD in palm oil mill effluent with 80% removal of COD in 2 h at pH 3 [17]. Olive mill wastewater has also been reportedly treated by Fenton with zero valent iron (ZVI) with COD removal of 92% at pH 2 to 4 [18]. Ultrasonic treatment itself is a novel oxidation technology to be used as effective •OH radical producer, the stronger oxidation potential specie for water [19]. Since ultrasonic due to its cavitation effect can provide synergistic effect in Fenton process [20]. Recently combination of ultrasonic technology and Fenton with magnetite particles has also been reported as not only because of their easy recovery due to magnetic effect but also because magnetic based catalysts are getting famous in heterogenous Fenton which is favourable in near neutral conditions [21]. Heterogenous Fenton in presence of micro ZVI as a catalyst has twofold benefits as compared with NZVI which is exhausted too fast [22].

The aim and objectives of this research is to apply ZVI based Fenton with additional exposure of sonication in near neutral conditions as to mimic sono-Fenton treatments for degradation of HA in SW as a pretreatment for MD. Design of experiments was made while changing concentration of H_2O_2, pH and quantity of ZVI. Results showed meaningful outcomes and relationships which are discussed in detail in section 3.

2. Material and methods

2.1. Experimental chemicals

All chemicals used in these experiments were reagent grade and extra pure. Hydrogen peroxide, anhydrous calcium chloride, strontium chloride hexahydrate, sodium bicarbonate, potassium bromide, boric acid, sodium fluoride and hydrochloric acid were purchased from Daejung Chemical, South Korea.

Potassium chloride, HA and sodium hydroxide were purchased from Sigma-Aldrich. Magnesium chloride hexahydrate was purchased from Samchun, South Korea. The commercial granular ZVI of 40 mesh, 0.6 mm diameter (Sang-Ah Blast, Korea) was used. The ZVI granules contain 98.83% of Fe, 0.85% of Si, 0.18% of C and minor impurities of Mn, P and S.

2.2. Equipment

For total organic carbon (TOC) analysis, Shimadzu TOC analyzer (TOC-L CPH 638-91112-58, Japan) was used which was calibrated with standard procedure given in catalogue of the instrument. SW and HA solution was mixed by magnetic plate stirrer (SMHS-6, Wise-Stir) and sono-Fenton with sonication was carried out on JAC Ultrasonic bath (4020P, KODO) having frequency of 40 kHz and power of 400–500 W. Finally, filtration was carried out through vacuum filtration device (J070346, South Korea) before measuring TOC.

2.3. Experimental design

In this study, experimental design was made as given in Table 1. All the experiments were then carried out with those recipes suggested by RSM for future design of process. Central composite design which is mostly used by many researchers before was chosen with two input factors and one output factor. Input factors were set as concentration of hydrogen peroxide and quantity of ZVI while output factor was degradation percentage in form of TOC removal. Table 1 further shows in detail set of experiments with different combinations of hydrogen peroxide and ZVI treatments. In addition to this, some extra experiments were carried out to check the effect of pH from 6 to 8.2 to evaluate the performance of this process. All those experiments were carried out for degradation of HA artificially contained in SW. For the purpose, artificial SW was prepared by using ASTM D-1141 (reapproved 203) method in deionized water and HA was added as this is one of the major component in natural organic matters and behaves as organic foulants. The concentration of HA was kept 25 mg/L in the final SW sample. However, pH in the range of 6–8.2 was set by using dilute solutions of HCl and NaOH.

Table 1
Design of experiments

S. no	ZVI (g/L)	H_2O_2 mM	pH
1	1	10	8.2
2	1	20	6
3	1	20	8.2
4	2	0	8.2
5	2	10	8.2
6	2	20	8.2
7	2	20	7
8	2	20	8.2
9	2	40	8.2
10	4	20	6
11	4	20	8.2
12	4	40	6
13	8	20	6
14	8	20	8.2

2.4. Experimental procedure

Synthetic SW was prepared by using ASTM D-1141 (reapproved 203) method and then was properly mixed with HA on magnetic stirrer before starting each experiment. Initial temperature in sonication bath was set at 25°C as to mimic natural SW. Every glass bottle, flask and beaker were washed with DI water before and after treatment and sampling. Each sample to be treated was made in volume of 500 mL of SW solution in 1 L beaker size to be treated. Following set of experiments given in Table 1, given concentrations of ZVI, H_2O_2 were put in beaker containing SW with HA. Then this beaker was treated in sonication bath for 30 min. Sampling was done for TOC test during different time intervals to check effect of time on process after 2, 5, 10, 15, 20 and 30 min each. Each sample was taken in same volume of 40 mL as to keep similarity in sampling and evaluation. All those samples were then filtered with vacuum filtration device using PVDF membrane filters (pore size 0.45 µm, made by Durapore, Merck Millipore Ltd. Ireland). The steps of experimental process are shown in Fig. 1 from preparation of sample up to process. However, filtration of samples taken after selected times and TOC was evaluated by TOC analyzer after then.

3. Results and discussions

3.1. Effect of pH on TOC removal

Fig. 2 shows the effect of pH on TOC removal in terms of HA degradation. This depicts that when pH 6 a slightly acidic was kept, the highest one of 63% TOC was removed while the highest one for pH 8.2 was 37%. Hence pH 6 is 26% more efficient for TOC removal in case when there is 25 mg/L HA than slightly alkaline pH in case of 20 mM H_2O_2 as shown in Fig. 1. This data was taken when amount of ZVI is 1 g/L. Hence, pH adjustment must be done towards acidic if high efficiency is required. However, for further investigation and effect of change in hydrogen peroxide concentration was done which is also shown in Fig. 2. That is also shown from Fig. 1 that changing concentration has not more favourable effect as the excessive concentration of hydrogen peroxide upto 40 mM can reduce the performance may be by iron ion scavenging effect, while reduced concentration of 10 mM had limited oxidation effect that may be due to less concentration of Fe^{2+} produced at that concentration of H_2O_2. Also Fig. 3 shows further effect of pH on TOC reduction when ZVI is 2 g/L and pH was changed at 6, 7 and 8 for each sample separately and same process was carried out. The results from Fig. 3 depicts that in this case, when pH was increased from 6 to 8.2, TOC reduction decreased. As when pH was 8.2, the maximum TOC reduction was 38.89% after 30 min. However, the optimum TOC reduction was 66.7% when pH was 6, while increasing pH to 7, TOC reduction percentage was also reduced around 2%. This shows that the performance of the process is better in pH 6.

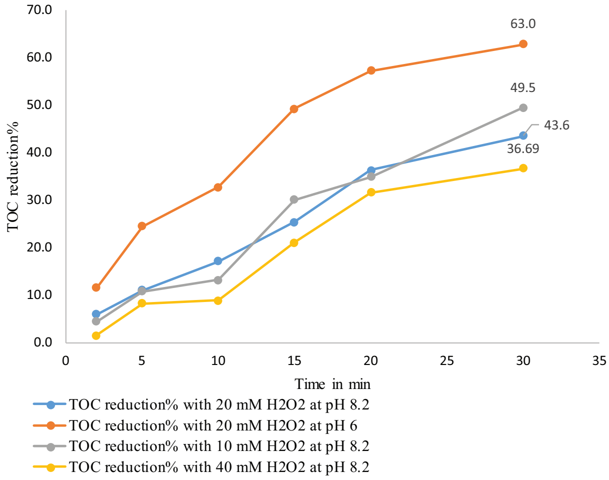

Fig. 2. Effect of pH on TOC removal at ZVI 1 g/L.

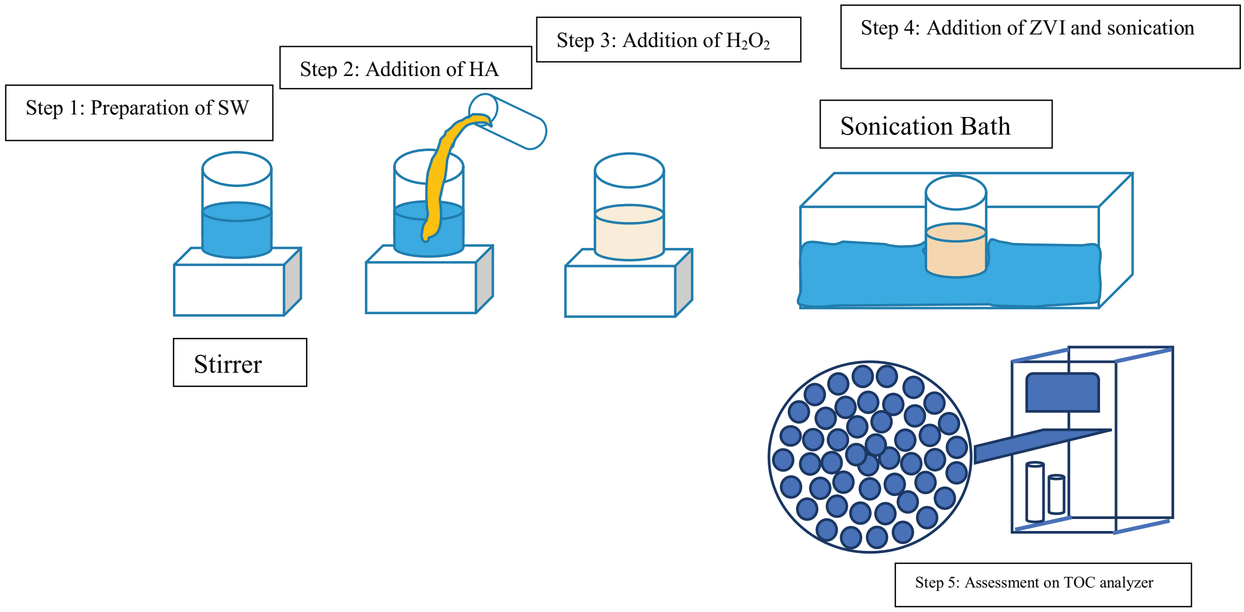

Fig. 1. Experimental setup for ZVI based sono-Fenton treatment of SW with HA.

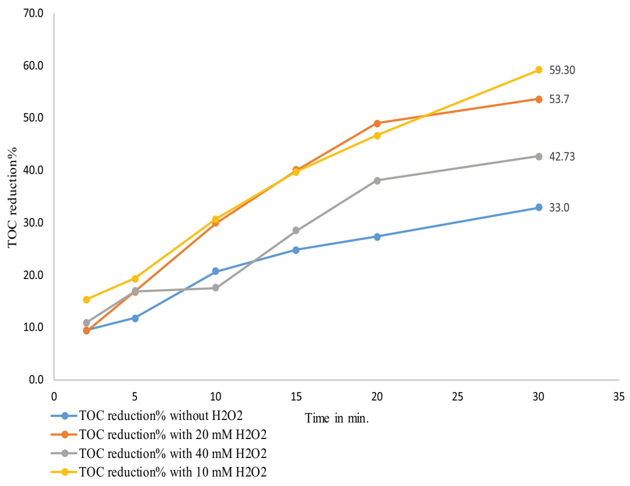

Fig. 3. Effect of pH on TOC removal at ZVI 2 g/L.

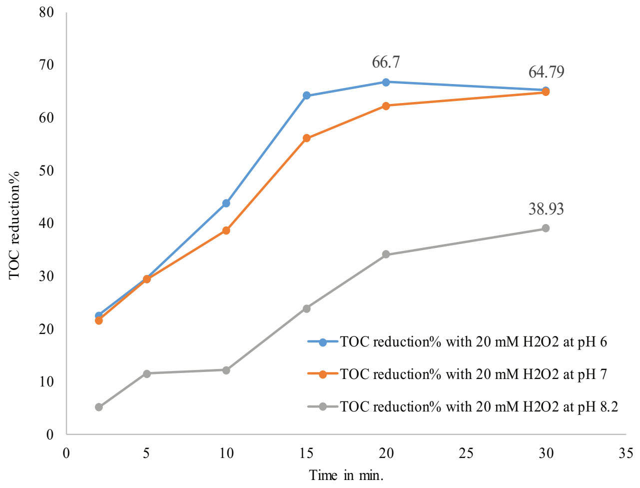

Fig. 4. Effect of concentration of H_2O_2 on TOC removal.

3.2. *Effect of concentration of H_2O_2 on HA degradation at different pH*

H_2O_2 plays key role in performance of Fenton reaction. Fig. 4 shows effect of changing concentration of H_2O_2 over TOC removal while keeping pH and amount of ZVI same. The pH was kept 8.2 and amount of ZVI was 2 g. The highest TOC reduction when there is no H_2O_2 is 33% which is 26.7% less than the optimum one which is 10 mM H_2O_2 by which TOC removal of 59.3% is reached . However, by increasing further concentration of hydrogen peroxide, TOC removal is increased but which is less efficiently. This reduced TOC removal especially in case of 40 mM H_2O_2 may be due to scavenging effect of H_2O_2. This suggests that here optimized concentration of H_2O_2 is 10 mM when pH is 8.2.

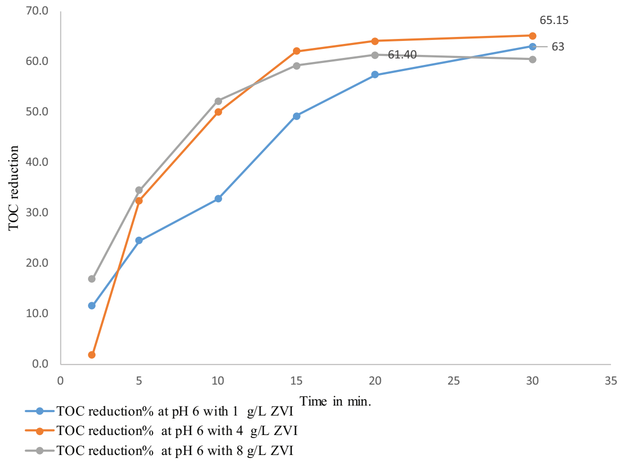

Fig. 5. Effect of increase in ZVI on TOC removal at pH 6.

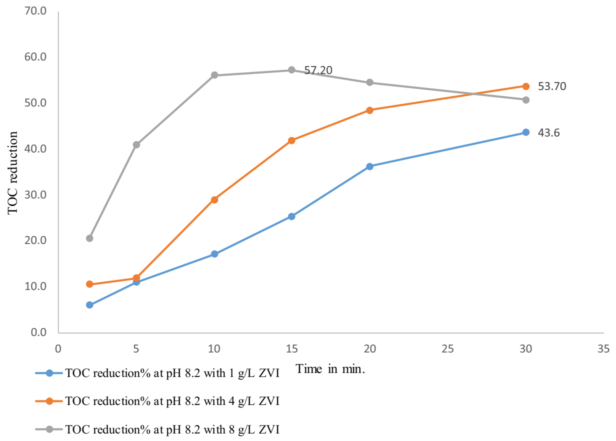

Fig. 6. Effect of increase in ZVI on TOC removal at pH 8.2.

3.3. *Effect of amount of ZVI on HA degradation*

Fig. 5 shows effect of increasing ZVI quantity with 20 mM concentration of H_2O_2 while keeping pH 6. This depicts that increasing quantity of ZVI has increased TOC reduction maximum up to 63% in case when ZVI is 1 g and 65.15% when ZVI is 4 g. However, further increase has resulted in rapid reduction up to 61.4% after that its efficiency decreases. This could be because of excessive concentration of Fe^{2+} ions produced from increasing amount of ZVI which has immediate consumption of H_2O_2. Or due to scavenging effect of Fe^{2+} ion by excessive H_2O_2 produced by ZVI itself.

Furthermore, Fig. 6 depicts the effect of increasing ZVI with 20 mM concentration of H_2O_2 while keeping pH 8.2. This shows that maximum TOC reduction when ZVI is 1 g is 43.6%, while it reaches 53.7% when amount of ZVI is increased up to 4 g. However, further increase of when ZVI is 8 g gives rapid TOC reduction within 15 min of maximum up to 57.2% which after this time declines. This could also be as the probable reason mentioned before, when ZVI is increased, it can increase H_2O_2 concentration that leads to scavenging effect.

4. Conclusions

In this study, it was asserted as in previous studies that ZVI is comparatively better than iron oxides to be used as catalyst in Fenton process as this release Fe^0 in controlled pattern which are converted into Fe^{2+} and Fe^{3+}. This is shown as continuous reduction of TOC shows the catalyst ion generation in order. ZVI based sono-Fenton with different concentrations of hydrogen peroxide has successfully reduced up to 67% HA degradation and TOC reduction. This is achieved by using 2 g/L of ZVI with 20 mM H_2O_2 at pH 6. However further variations in concentrations of ZVI, pH and H_2O_2 can formulize optimize conditions for lower or higher concentrations of HA in SW.

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